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(54) PROCESS FOR MANUFACTURING PAPER HAVING IMPROVED DRY STRENGTH

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ABSTRACT OF THE DISCLOSURE

Paper having improved dry strength is manufactured from a composition produced by mixing a pulp slurry with a water soluble cationic polymer and then, adding a water soluble anionic polymer to the slurry.

The present invention relates to a process for manufacturing paper. More particularly, the invention relates to a process for improving dry strength of paper with a cationic polymer and an anionic polymer.

It is important to improve paper strength because hardwood pulp providing lower paper strength must be used as the raw material because of a shortage of softwood pulp providing higher paper strength. It is known to add a water soluble polymer, such as starch, in the paper manufacture in order to improve the dry paper strength. It is considered that the starch is an adhesive between pulp fibers. However, starch is easily removed in the white water in the paper making process and the use of strength agents as dry anionic polymers has increased. When the anionic polymers are used, the polymers are retained on pulp fibers as water insoluble particles formed by adding aluminum sulfate.

A method of improving the retention by adding the anionic polymer and aluminum sulfate and then adding a water soluble cationic polymer to cause aggregation of the water insoluble particles formed in the deposition of the anionic dry strength agent with aluminum sulfate, has been disclosed in TAPPI Vol. 51 No. 11, 59A - 65A(1968). A method of simultaneously adding the water soluble anionic polymer and the water soluble cationic polymer is also disclosed in said reference. In the method, coarse particles formed by reaction in water are deposited on the surface of the pulp. However, on the basis of the adhesive concept, the dry strength agent acting as an adhesive agent should maximize the contact area of pulp fibers. Accordingly, it is preferably to uniformly cover the surface of the pulp fiber with fine particles in comparison with coarse particles between the pulp fiber.

In the aforesaid methods, the water soluble anionic polymer may be ununiformly distributed on the surface of the

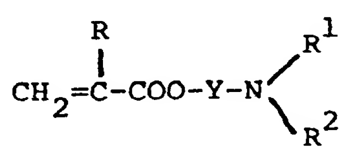
pulp fiber and as a result, the improvement in dry paper strength has not been sufficiently high.

It has now been found that dry paper strength can be improved by sequentially adding the water soluble cationic polymer and then the water soluble anionic polymer.

Thus the present invention provides for improving dry paper strength in the manufacture of paper.

According to the present invention there is provided a process for manufacturing paper having improved dry strength which comprises mixing an essentially alum free pulp slurry with a water soluble cationic polymer and subsequently adding a water soluble anionic polymer to the essentially alum free slurry and making the paper from the composition so obtained.

The water soluble cationic polymers used in the process of the present invention include various polymers as homopolymers of a cationic monomer or copolymers of at least one cationic monomer and another unsaturated compound. Suitable cationic monomers include vinylpyridine; vinylimidazolidien; diallylamine; ethyleneimine; and acrylates and methacrylates having the formula



wherein R represents hydrogen atom or methyl group; R^1 and R^2 are the same or different and represent an alkyl group or an aralkyl group and Y represents an alkylene group having 2 or more of carbon atoms or a hydroxylalkylene group having 2 ~~or~~ more of carbon atoms; such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dibutylaminoethyl acrylate, dibutylaminoethyl methacrylate, methylethylaminoethyl acrylate, and dimethylamino-2-hydroxypropyl methacrylate, and acid salts of

the cationic monomers. The acids used for the acid salts can be inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid and organic acids such as acetic acid and propionic acid. The cationic monomers can be also quaternary ammonium salts of said cationic monomers obtained by reacting said cationic monomer with a quaternizing agent such as an alkyl halide, an aralkyl halide or a dialkyl sulfate. Other suitable unsaturated compounds used for copolymerizing with said cationic monomer include acrylamide or methacrylamide.

The water soluble cationic polymers can be also cationic modifiers of polymers having main component of acrylamide or methacrylamide (hereinafter referring to cationic modified acrylamide polymer). The cationic modified acrylamide polymers can be a Mannich reaction product obtained by reacting the acrylamide polymer with formaldehyde and an amine such as (methylamine, dimethylamine, ethylamine, or diethylamine) and aminomethylating a part of carbamoyl groups of the polymer; modified polymers obtained by converting a part of carbamoyl groups of the polymer to amino group by Hofmann degradation; and quaternary compounds obtained by reacting said Mannich reaction product with the quaternizing agent. The water soluble cationic polymers can be also cationic polycondensates such as polycondensates of an epoxy compound such as epihalohydrin with at least one of amines such dimethylamine, monoethylamine, ethylenediamine, polyalkylene polyamines such as pentalthylene hexamine, polyamide polyamine, aniline and ammonia (USP 3,738,945) and polycondensates of formaldehyde and said amine or dicyandiamide. The water soluble cationic polymers can be also cationic modified high molecular natural compounds such as cationic modified starch and glycolchitosan. The optimum water soluble cationic polymers include homopolymers of diallylamine, or quaternary salts thereof, dimethyl aminoethyl methacrylate, or

quaternary salts salts thereof; and copolymers of the monomer with acrylamide; partial Mannich reaction products of acrylamide polymer and quaternary ammonium compounds thereof and polycondensates of epichlorohydrin and dimethyl amine. It is especially preferable to use the quaternary ammonium compound since it can be added regardless of pH of the pulp slurry.

The retention of the water soluble cationic polymer used in the process of the present invention increases with the increase of molecular weight of the water soluble cationic polymer and it is preferably to be of high molecular weight. In the process of the present invention, it is necessary that the viscosity of 10% aqueous solution of the water soluble cationic polymer be greater than about 5 cps, preferably greater than about 10 cps. The content of the cationic groups in the polymer affects to the effect of retention. The optimum cation content depends upon the molecular weight of the polymer and is usually greater than about 1.0 gram ion/Kg. polymer for the polymer having greater than about 100 cps of viscosity for a 10% aqueous solution and is usually greater than about 3.0 gram ion/Kg. polymer for the polymer having 5 to 100 cps of viscosity for a 10% aqueous solution.

The amount of the water soluble cationic polymer depends upon the types of the pulp and the cationic polymer and the dry strength of the desired paper, and is usually more than about 0.01% by weight per dry pulp. The amount of the water soluble cationic polymer can be increased until ~~flo~~ating the polymer in water without the retention on the pulp fiber to cause the decrease of the paper strength. The maximum dosage depends upon the type of pulp and the water soluble cationic polymer and is usually about 1 wt.% per dry pulp.

The water soluble anionic polymers used in the present invention can be various anionic polymers used as dry strength

agent. ("Strength agents" in Paper and Pulp Technology Times in Japan: Oct. 1976). Suitable water soluble anionic polymers include the polymers having carboxyl groups or carboxylate groups such as partially hydrolyzed products of acrylamide polymers and salts thereof, copolymers of acrylamide and maleic acid, acrylic acid or salt thereof; and oxidized starch. It is also possible to use water soluble polymers having sulfonic acid group. The anionic polymers having a viscosity of about less than 50,000 cps as a 10% aq. sol. are preferably used. An anion component in the water soluble anionic polymer is in a range of 2 to 30 mole %, preferably 4 to 25 mole % as acrylic acid in the case of the copolymer of acrylamide and acrylic acid. The conversion ratio of hydrolysis is in a range of 2 to 30 mole %, preferably 4 to 25 mole % in the case of partially hydrolyzed product of polyacrylamide wherein the mole % designates the ratio of the hydrolyzed monomer component in total monomer components in the polymer. The anion content corresponds to 0.280 to 3.85 gram ion/Kg. polymer preferably 0.556 to 3.26 gram ion/Kg. polymer as the unit of gram ion. In the other water soluble anionic polymer, the anion content may be selected from said range.

The amount of the water soluble anionic polymer is the amount used as the conventional dry strength agent and depends upon the types of the pulp and the anionic polymer and the desired dry strength agent and is usually more than about 0.1% by weight to dry pulp. The ionic equivalent ratio of the water soluble cationic polymer to the water soluble anionic polymer is more than about 10 mole % preferably more than about 50 mole %.

In the paper manufacture by the process of the present invention, it is necessary to add the water soluble cationic polymer to the pulp slurry first and then to add the water soluble anionic polymer The water soluble cationic polymer and the

water soluble anionic polymer are added to the pulp slurry in a desirably stage from the preparation of the pulp slurry to the formation of paper sheet, that is, from the preparation of pulp slurry composition to the wet end on a paper machine wire.

The preparation of the paper slurry composition can be attained by conventional processes except sequentially adding the water soluble cationic polymer and the water soluble anionic polymer in that order.

The pulp used in the paper manufacture is not critical and can be hard wood and soft wood or regenerated pulp obtained from waste paper. It is possible to add the conventional additives such as filler, a sizing agent, a dyestuff and other additive as desired. The additives can be the conventional ones used in the conventional paper manufacture such as kaolin, talc, clay, calcium carbonate and titanium oxide as the filler; rosin sizing agent and synthetic sizing agent as the sizing agent. The additives can be added before or after the addition of the water soluble cationic polymer and the water soluble anionic polymer. If necessary, aluminum sulfate can be subsequently added in order to improve the retention of the water soluble cationic polymer and anionic polymer and the additives. The pH of the pulp slurry may be controlled in a range of 4 to 9 as the conventional process. In the optimum example for prearing the pulp slurry, the water soluble cationic polymer is added and dispersed to the pulp slurry with or without a filler and then, the water soluble anionic polymer is added and then a rosin sizing agent is added, and finally, aluminum sulfate is added. The paper making of the pulp slurry can be attained by the conventional process.

The important feature of the present invention is to add the water soluble cationic polymer to the pulp slurry to charge the surface of the pulp fiber in positive charged and then, to add the water soluble anionic polymer to uniformly distribute the

anionic polymer on the surface of the pulp fiber. When the cationic polymer is added after the addition of the anionic polymer or at the same time adding the anionic polymer as the conventional process, the effect of the present invention is not achieved.

When aluminum sulfate is used instead of the water soluble cationic polymer in order to give the positive charge on the surface of pulp fiber, the adsorption of aluminum sulfate on the pulp is weak whereby it is not possible to provide enough positive charge. When a large amount of aluminum sulfate is added, aluminum ions remain in water to react aluminum sulfate with the anionic polymer whereby the water insoluble particles are disadvantageously produced. On the contrary, the water soluble cationic polymer is completely retained on the surface of the pulp fiber by vigorously stirring even though a large amount of the cationic polymer is added.

Accordingly, the anionic polymer added later, can be completely retained on the surface.

The present invention will be further illustrated by way of the following examples in which

(a) The dry strength was measured by Japanese Industrial Standard as bursting factor and comprehensive strength.

(b) The viscosity of the polymer was shown as the viscosity of 10% aqueous solution of the polymer measured at 25°C by Brookfield viscometer, and

(c) The ion content was shown in the unit of gram ion/Kg. polymer.

Example 1:

A water soluble cationic polymer (A), a water soluble anionic polymer (B) and aluminum sulfate (C) were respectively added, in the order shown in Tables, to 0.5% of a pulp slurry of LBKP (Hardwood bleached kraft pulp) beaten to CSF (Canadian

Standard Freeness) of 400 ml.

The resulting pulp slurry was treated by TAPPI standard sheet machine to make a paper having a basis weight of 50g/m^2 and the bursting factor of the paper was measured by Japanese Industrial Standard P-8112.

The results are shown in Tables 1 to 3.

The kinds of the polymers and aluminum sulfate and the stirring condition are as follows.

Water soluble cationic polymer (A):

Copolymer having 70 mole % of acrylamide component and 30 mole % of methacryloyloxyethyl trimethyl ammonium chloride component which had a viscosity of 9800 cps and a cation content of 2.68 gram ion/Kg. polymer.

Water soluble anionic polymer (B) :

Partially hydrolyzed product of polyacrylamide which had a hydrolysis rate of 15 mole % and a viscosity of 12,000 cps and anion content of 2.02 gram ion/Kg.polymer.

Aluminum sulfate (C): Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components (A),(B) and (C). The amounts of the components are shown as percentages per dry pulp.

Table 1:(Reference)

Order of addition : Component (B)→Component (C)

(A)%	(B)%	(C)%	Bursting factor
0	0.1	2.0	2.83
0	0.2	2.0	3.15
0	0.3	2.0	3.31
0	0.4	2.0	3.48

Table 2 : (Reference)

Order of addition : Component (B)⟶Component (C)⟶Component (A)

(A)%	(B)%	(C)%	Bursting factor
0.01	0.2	2.0	3.21
0.03	0.2	2.0	3.25
0.06	0.2	2.0	3.35
0.10	0.2	2.0	3.50

Table 3: (Invention)

Order of addition: Component(A)→Component(B)→Component (C)

(A) %	(B)%	(C)%	Bursting factor
0.01	0.2	2.0	3.23
0.03	0.2	2.0	3.48
0.06	0.2	2.0	3.72
0.10	0.2	2.0	3.96

In comparison with the results in Tables 1 and 2, the paper made by the process of the present invention had significantly high strength as shown in Table 3.

Example 2:

A water soluble cationic polymer (A^1) was added and mixed to 0.5% of a pulp slurry of wasted corrugated board beaten to CSF of 400 ml and then, a water soluble anionic polymer (B^1) was added. The resulting pulp slurry was treated by TAPPI standard sheet machine to make a paper having a basis weight of 150g/m^2 and the compressive strength of the paper was measured by Japanese Industrial Standard P-8126. The results are shown in Table 5.

As the reference, the water soluble anionic polymer (B^1) and aluminum sulfate (C) were added and the resulting pulp slurry was treated to make a paper. The results are shown in Table 4. The kinds of the polymers are as follows.

Water soluble cationic polymer (A^1):

Quaternary ammonium compound of Mannich reaction product obtained by reacting polyacrylamide with formamide and dimethylamide, then quaternized with dimethyl sulfate.

Dimethyl aminomethylated component: 50 mole % to acrylamide component

Quaternary component: 30 mole % to acrylamide component

Viscosity : 13,500 cps

Cation content : 3.51 gram ion/Kg. polymer

Water soluble anionic polymer (B^1):

Copolymer of 10 mole % of sodium acrylate and 90 mole % of acrylamide

Viscosity: 8,000 cps (10 % aq.)

Anion content: 1.37 gram ion/Kg. polymer

Aluminum sulfate: Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components (A^1), (B^1) and (C). The amounts of the components are shown as percentages per dry pulp.

Table 4:(Reference)

Order of addition: Components $(B^1) \rightarrow (C)$

(A^1)%	(B^1)%	(C)%	Compressive strength (Kg. f)
0	0.2	0	15.2
0	0.3	0	1.52
0	0.4	0	15.5
0	0.2	2.0	17.5
0	0.3	2.0	18.4
0	0.4	2.0	19.3
0	0.2	3.0	17.6
0	0.3	3.0	18.6
0	0.4	3.0	19.3

Table 5: (Invention)

Order of addition: Components $(A^1) \longrightarrow (B^1) \longrightarrow (C)$

(A^1)%	(B^1)%	(C)%	Compressive strength (Kg. f)
0.01	0.2	0	20.1
0.03	0.2	0	20.5
0.06	0.2	0	21.3
0.10	0 2	0	22.5
0.01	0.3	0	20.6
0.03	0 3	0	21.5
0.06	0.3	0	22.8
0.10	0.3	0	23.4
0.01	0.4	0	21.1
0.03	0.4	0	22.6
0.06	0.4	0	23.5
0.10	0.4	0	24.5
0.01	0.2	2	20.8
0.03	0.2	2	21.4
0.06	0.2	2	22.2
0.1	0.2	2	22.8
0.01	0.3	2	21.2
0.03	0.3	2	21.8
0.06	0.3	2	22.6
0.1	0.3	2	23.1
0.01	0.4	2	21.7
0.03	0.4	2	22.4
0.06	0.4	2	23.0
0.1	0.4	2	23.5

Example 3:

A water soluble cationic polymer $(A^2 - 1)$, $(A^2 - 2)$ and a water soluble anionic polymer (B^2) and aluminum sulfate (C) and a sizing agent (D) were added to 5 % of a pulp slurry of LBKP having CSF of 400 ml in various orders . The resulting pulp slurry was treated to make a paper in accordance with the process of Example 1 and the

bursting factor of the paper was measured. The results are shown in Tables 6 to 8.

Table 6 shows the results of the cases using no water soluble cationic polymer.

Table 7 shows the results of the cases using the water soluble cationic polymer (A^2 - 2) having low viscosity such as 3 cps. (10% aq.) Even though the order of additions is (A^2 - 2) $\longrightarrow$ (B) $\rightarrow$ (D) $\rightarrow$ (C), the results were not superior.

Table 8 shows the results of the cases using the water soluble cationic polymer having a viscosity of 12 cps.

Water soluble cationic polymer (A^2 - 1):

Reaction product of epichlorohydrin and ethylenediamine at equi-molar ratio

Viscosity: 12 cps (10% aq)

Cation content: 13.1 gram ion/Kg·polymer

Water soluble cationic polymer (A^2 - 2):

The same with (A^2 - 1)

Viscosity : 3 cps (10% aq)

Cation content: 13.1 gram ion/Kg·polymer

Water soluble anionic polymer (B^2):

Partially hydrolyzed product of polyacrylamide having 15 mole % of anionic component content.

Viscosity : 12,000 cps

Aluminum sulfate (C): Solid aluminum sulfate

Sizing agent (D):

Enriched rosin size Sizepine E (Manufactured by Arakawa Kagaku K.K.)

Stirring condition:

Each stirring by a propeller stirrer was carried out at 100 r.p.m. for 30 seconds after each addition of each of component (A^2 -1), (A^2 - 2), (B^2), (D), (C). The amounts of the components are

shown as percentages per dry pulp.

Table 6:(Reference)

Order of addition: Components $(B^2) \rightarrow (D) \rightarrow (C)$

(B^2)%	(D)%	(C)%	Bursting factor
0.1	1.0	3.0	3.02
0.2	1.0	3.0	3.23
0.3	1.0	3.0	3.33

Table 7:(Reference)

Order of addition: Components $(A^2\text{-}2) \rightarrow (B^2) \rightarrow (D) \rightarrow (C)$

$(A^2\text{-}2)$%	(B^2)%	(D)%	(C)%	Bursting factor
0.01	0.2	1.0	3.0	3.30
0.05	0.2	1.0	3.0	3.36
0.10	0 2	1.0	3.0	3.43

Table 8: (Invention)

Order of addition: Components $(A^2\text{-}1) \rightarrow (B^2) \rightarrow (D) \rightarrow (C)$

$(A^2\text{-}1)$%	(B^2)%	(D)%	(C)%	Bursting factor
0.01	0.1	1.0	3.0	3.32
0.05	0.1	1.0	3.0	3.49
0.10	0.1	1.0	3.0	3.62
0.01	0.2	1.0	3.0	3.45
0.05	0.2	1.0	3.0	3.61
0.10	0.2	1.0	3.0	3.78
0.01	0.3	1.0	3.0	3.68
0.05	0.3	1.0	3.0	3.80
0.10	0.3	1.0	3.0	3.95

Example 4:

A filler (E) was added to 0.5 % of a pulp slurry of LBKP having CSF of 400 mL and then, a water soluble cationic poly-

mer (A^3) was added and then, a water soluble anionic polymer (B^3) was added and the sizing agent (D) was added, and aluminum sulfate (C) was added. The resulting pulp slurry was treated by TAPPI standard sheet machine to make a paper having a basis weight of 50 g/m^2 and the bursting factor of the paper was measured by Japanese Industrial Standard P-8112.

The results are shown in Table 11.

Table 9 shows the results of the cases using no water soluble cationic polymer (A^3).

Table 10 shows the results of the cases adding the water soluble cationic polymer (A^3) after the addition of aluminum sulfate (C).

The amounts of the components are shown as percentages per dry pulp.

Water soluble cationic polymer (A^3):

Copolymer of 60 mole % of acrylamide component and 40 mole % of dimethyl aminoethyl methacrylate.

Viscosity : 2300 cps (10% aq.)

Cation content : 4.01 gram ion/Kg.polymer

Water soluble anionic polymer (B^3) :

Partially hydrolyzed product of polyacrylamide

Anionic component : 20 mole %

Viscosity : 35,000 cps (10 % aq.)

Anion content : 2.65 gram ion/Kg. polymer

Sizing agent (D) : Enriched rosin size Sizepine E

Aluminum sulfate (C) : Solid aluminum sulfate

Filler (E) : Talc for paper making

Stirring condition :

Each stirring by a propeller stirrer was carried out at 100 r.p.m. for 30 seconds after each addition of each of components (A^3), (B^3), (C), (D), (E).

The amounts of the components are shown as percentages per dry pulp.

Table 9 : (Reference)

Order of addition :Components (E)$\rightarrow$(B^3)$\rightarrow$(D)$\rightarrow$(C)

(E)%	(B^3) %	(D)%	(C)%	Bursting factor
15	0.1	1.0	5.0	1.92
15	0.2	1.0	5.0	2.08
15	0.3	1.0	5.0	2.21

Table 10:(Reference)

Order of addition: Components (E)$\rightarrow$(B^3)$\rightarrow$(D)$\rightarrow$(A^3)

(E)%	(B^3)%	(D)%	(C)%	(A^3)%	Bursting factor
15	0.1	1.0	5.0	0.01	1.98
15	0.1	1.0	5.0	0.05	2.05
15	0.1	1.0	5.0	0.10	2.14
15	0.3	1.0	5.0	0.01	2.27
15	0.3	1.0	5.0	0.05	2.32
15	0.3	1.0	5.0	0.10	2.40

Table 11:(Invention)

Order of addition: Components (E)$\rightarrow$(A^3)$\rightarrow$(B^3)$\rightarrow$(D)$\rightarrow$(C)

(E)%	(A^3)%	(B^3)%	(D)%	(C)%	Bursting factor
15	0.01	0.1	1.0	5.0	2.15
15	0.05	0.1	1.0	5 0	2.34
15	0.10	0.1	1.0	5.0	2.58
15	0.01	0.3	1.0	5.0	2.49
15	0.05	0.3	1.0	5.0	2.60
15	0.10	0.3	1.0	5.0	2.77

Example 5:

The process of Example 1 was repeated under the following conditions.

Pulp: Mixture of NUKP (Softwood unbreached kraft pulp) and LUKP (Hardwood unbreached kraft pulp (1:1) having CSF of 350 ml.

Basis weight of paper : 60 g/m^2

Water soluble cationic polymer (A^4):

Homopolymer of dimethyldiallyl ammonium chloride :
Viscosity : 800 cps (10 % aq.)
Cation content : 5.99 gram ion/Kg·polymer

Water soluble anionic polymer (B^4):

Partially hydrolyzed product of polyacrylamide :
Hydrolyzed component : 8 mole %
Viscosity : 11300 cps (10 % aq.)
Anion content : 1.10 gram ion/Kg· polymer

Aluminum sulfate (C) : Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components (A^4), (B^4), (C). The amount of the components are shown as percentages per dry pulp.

Table 12 : (Reference)

Order of addition : Components (B^4) $\longrightarrow$ (C)

$(A^4)\%$	$(B^4)\%$	$(C)\%$	Bursting factor
0	0.1	1.5	3.13
0	0.2	1.5	3.36
0	0.3	1.5	3.58
0	0.4	1.5	3.80
0	0.1	0	2.91
0	0.2	0	2.93
0	0.3	0	2.96
0	0.4	0	2.99

Table 13: (Reference)

Order of addition: Components $(B^4) \longrightarrow (C) \longrightarrow (A^4)$

$(A^4)\%$	$(B^4)\%$	$(C)\%$	Bursting factor
0.01	0.2	1.5	3.39
0.03	0.2	1.5	3.46
0.06	0.2	1.5	3.55
0.1	0.2	1.5	3.63
0.01	0.3	1.5	3.61
0.03	0.3	1.5	3.69
0.06	0.3	1.5	3.76
0.1	0.3	1.5	3.75
0.01	0.2	0	3.00
0.03	0.2	0	3.07
0.06	0.2	0	3.15
0.1	0.2	0	3.23
0.01	0.3	0	3.08
0.03	0.3	0	3.15
0.06	0.3	0	3.23
0.1	0.3	0	3.41

Table 14: (Invention)

Order of addition: Components (A^4) ⟶ (B^4) ⟶ (C)

(A^4)%	(B^4)%	(C)%	Bursting factor
0.01	0.2	1.5	3.45
0.03	0.2	1.5	3.59
0.06	0.2	1.5	3.71
0.1	0.2	1.5	3.84
0.01	0.3	1.5	3.67
0.03	0.3	1.5	3.79
0.06	0.3	1.5	3.90
0.1	0.3	1.5	4.02
0.01	0.2	0	3.13
0.03	0.2	0	3.35
0.06	0.2	0	3.58
0.1	0.2	0	3.80
0.01	0.3	0	3.25
0.03	0.3	0	3.43
0.06	0.3	0	3.69
0.1	0.3	0	3.98

Example 6:

The process of Example 1 was repeated under the following conditions.

Pulp: Wasted corrugated board beaten to give CSF of 300 ml

Basis weight of paper: 70 g/m^2

Water soluble cationic polymer (A^5):

Polyethyleneimine:

Viscosity: 8 cps (10 % aq.)

Cation content : 23.3 gram ion /Kg·polymer

Water soluble anionic polymer (B^5)

Partially hydrolyzed product of polyacrylamide:

Anionic component : 15 mole %

Viscosity: 12000 cps (10 % aq.)

Anion content: 20.2 gram ion /Kg·polymer

Aluminum sulfate (C) : Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200

r.p.m. for 30 seconds after each addition of each of components (A^5), (B^5), (C). The amounts of the components are shown as percentages per dry pulp.

Table 15: (Reference)

Order of addition: Components (B^5) ⟶ (C)

(A^5)%	(B^5)%	(C)%	Bursting factor
0	0.3	0.5	1.83
0	0.4	0.5	1.90
0	0.5	0.5	1.98
0	0.3	1.5	1.95
0	0.4	1.5	2.08
0	0.5	1.5	2.20

Table 16: (Invention)

Order of addition: (A^5) ⟶ (B^5) ⟶ (C)

(A^5)%	(B^5)%	(C)%	Bursting factor
0.03	0.3	0.5	1.92
0.06	0.3	0.5	2.04
0.1	0.3	0.5	2.19
0.03	0.4	0.5	2.01
0.06	0.4	0.5	2.18
0.1	0.4	0.5	2.30
0.03	0.3	1.5	2.03
0.06	0.3	1.5	2.15
0.1	0.3	1.5	2.26
0.03	0.4	1.5	2.13
0.06	0.4	1.5	2.25
0.1	0.4	1.5	2.37

Example 7:

The process of Example 1 was repeated under the following conditions.

Pulp: Mixture of wasted news-paper and wasted corrugated board (1 :1) beaten to give CSF of 220 ml.

Basis weight of paper: 80 g/m^2

Water soluble cationic polymer (A^6 - 1):

Copolymer of 85 mole % of acrylamide component and 15 mole % of methacryloyloxy ethyl trimethyl ammonium chloride component.

Viscosity: 9700 cps (10 % aq)

Cation content : 1.64 gram ion/Kg·polymer

Water soluble cationic polymer (A^6-2) :

Copolymer of 95 mole % of acrylamide component and 5 mole % of methacryloyloxy ethyl trimethyl ammonium chloride component.

Viscosity: 9550 cps (10% aq.)

Cation content:0.643 gram ion/Kg·polymer

Water soluble anionic polymer (B^6):

Partially hydrolyzed product of polyacrylamide

Anionic component: 15 mole %

Viscosity: 12000 cps (10 % aq.)

Anion content : 2.02 gram ion/Kg·polymer

Aluminum sulfate(C): Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components (A^6 -1) (A^6-2) (B), (C). The amounts of the components are shown as percentages per dry pulp.

Table 17:(Reference):

Order of addition : Components (B^6) →(C)

(B^6) %	(C)%	Bursting factor
0.3	15	1.61
0.4	15	1.69
0.5	15	1.77

Table 18:(Invention)

Order of addition: Components (A^8-1) or (A^6 - 2)⟶(B^6)⟶(C)

(A^6-1)%	(B^6)%	(C)%	Bursting factor
0.01	0.3	1.5	1.65
0.03	0.3	1.5	1.73
0.06	0.3	1.5	1.81
0.1	0.3	1.5	1.90
0.01	0.4	1.5	1.72
0.03	0.4	1.5	1.80
0.06	0.4	1.5	1.89
0.1	0.4	1.5	1.97

(A^6-1)%	(B^6)%	(C)%	Bursting factor
0.01	0.3	1.5	1.63
0.03	0.3	1.5	1.68
0.06	0.3	1.5	1.73
0.1	0.3	1.5	1.76
0.01	0.6	1.5	1.71
0.03	0.6	1.5	1.76
0.06	0.6	1.5	1.81
0.1	0.6	1.5	1.86

Since the cation content of (A^6-2) is lower than that of (A^6 -1), the former gives lower effect.

Example 8:

The process of Example 1 was repeated under the following conditions.

Pulp: LBKP having CSF of 350 ml.

Basis weight of paper : 60 g/m^2

Water soluble cationic polymer (A^7)

Quaternary ammonium compound of Mannich reaction product obtained by reacting polyacrylamide with formaldehyde and dimethyl-

amine then quaternized with dimethyl sulfate.

Amino component : 60 mole % to acrylamide component

Quaternary component : 32 mole % to acrylamide component

Viscosity : 4500 cps (10 % aq.)

Cation content : 3.89 gram ion/Kg.polymer

Water soluble anionic polymer (B^7)

Copolymer of 10 mole % of acrylonitrile, 10 mole % of sodium acrylate, 80 mole % of acrylamide.

Viscosity : 2300 cps (10 % aq.)

Aluminum sulfate (C): Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components (A^7), (B^7), (C). The amount of the components are shown as percentages per dry pulp.

Table 19 (Reference):

Order of addition: Components (B^7) $\longrightarrow$ (C)

(A^7)%	(B^7)%	(C)%	Bursting factor
0	0.3	1.5	2.16
0	0.5	1.5	2.34
0	1.0	1.5	2.53

Table 20: (Invention

Order of addition: Components (A^7) $\longrightarrow$ (B^7) $\longrightarrow$ (C)

(A^7)%	(B^7)%	(C)%	Bursting factor
0.03	0.1	1.5	2.30
0.06	0.1	1.5	2.42
0.1	0.1	1.5	2.54
0.03	0.3	1.5	2.51
0.06	0.3	1.5	2.67
0.1	0.3	1.5	2.79
0.03	0.5	1.5	2.61

0.06	0.5	1.5	2.80
0.1	0.5	1.5	3.01

Example 9:

The process of Example 1 was repeated under the following conditions.

Pulp: Mixture of LBKP and SCP (semi-chemical pulp) (1:1) having CSF of 280 ml

Basis weight of paper: 55 g/m^2

Water soluble cationic polymer (A^8 -1):

Homopolymer of dimethyl diallyl ammonium chloride

Viscosity: 30 cps (10 % aq.)

Cation content : 5.99 gram ion/Kg·polymer

Water soluble cationic polymer (A^8 -2):

Copolymer of 20 mole % of dimethyl diallyl ammonium chloride component and 80 mole % of acrylamide component.

Viscosity ; 33 cps (10 % aq.)

Cation content : 2.21 gram ion/Kg·polymer

Water soluble cationic polymer (A^8 -3):

Copolymer of 20 mole % of dimethyl diallyl ammonium chloride component and 80 mole % of acrylamide component.

Viscosity: 350 cps (10% aq.)

Cation content : 2.21 gram ion/Kg·polymer

Water soluble anionic polymer (B^8):

Partially hydrolyzed product of polyacrylamide

Anionic component : 10 mole %

Viscosity 8500 cps (10 % aq.)

Anion content :1.37 gram ion/Kg·polymer

Aluminium sulfate (C): Solid aluminum sulfate

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m. for 30 seconds after each addition of each of components

$(A^8-1), (A^8-2), (A^8-3), (B^8)$, (C).

The amounts of the components are shown as percentages per dry pulp.

Table 21(Reference):

Order of addition: Components $(B^8) \longrightarrow (C)$:

(A^8-1) (A^8-2) (A^8-3) %	(B^8)%	(C)%	Bursting factor
0	0.2	1.5	1.83
0	0.4	1.5	2.14
0	0.6	1.5	2.46

Table 22:(Invention)

Order of Addition: $(A^8-1), (A^8-2), (A^8-3) \longrightarrow (B^8) \longrightarrow (C)$:

(A^8-1)%	(B^8)%	(C)%	Bursting factor
0.03	0.2	1.5	1.98
0.06	0.2	1.5	2.16
0.1	0.2	1.5	2.30
0.03	0.4	1.5	2.28
0.06	0.4	1.5	2.45
0.1	0.4	1.5	2.60

(A^8-2)%	(B^8)%	(C)%	Bursting factor
0.03	0.2	1.5	1.90
0.06	0.2	1.5	1.96
0.1	0.2	1.5	2.01
0.03	0.4	1.5	2.21
0.06	0.4	1.5	2.27
0.1	0.4	1.5	2.32

(A^8-3)%	(B^8)%	(C)%	Bursting factor
0.03	0.2	1.5	1.97
0.06	0.2	1.5	2.14
0.1	0.2	1.5	2.28
0.03	0.4	1.5	2.25
0.06	0.4	1.5	2.42
0.1	0.4	1.5	2.57

Since the cation content of (A^8-2) is lower than that of (A^8-10) the effect of strengthening is inferior.

Since the viscosity of (A^8-3) is higher though the cation contents of (A^8-2) and (A^8-3) are the same, the effect of strengthening is superior.

Example 10 :

A water soluble cationic polymer (A^9), a water soluble anionic polymer (B^9) , a sizing agent (D), aluminum sulfate (C) were sequentially added to 0.5 % of pulp slurry of LBKP beaten to give CSF of 400 ml. in the order. The resulting pulp slurry was treated by TAPPI Standard Sheet Machine to make a paper having a basis weight of 50 g/m^2. The bursting factor of the paper was measured. The results are shown in Table 25.

As the reference, the cationic polymer (A^9) was not used, or the order of addition was changed and the bursting factor of the paper was measured. The results are shown in Tables 23 and 24.

The following components were used.

Water soluble cationic polymer (A^9):

Mannich compound of polyacrylamide
Cationic component : 50 mole %
Viscosity : 15,000 cps (10 % aq.)

Water soluble anionic polymer (B^9)

Partially hydrolyzed product of polyacrylamide
Hydrolyzed component: 11.3 mole %
Viscosity: 7,700 cps (10 % aq.)

Aluminum sulfate (C) : Solid aluminum sulfate

Sizing agent(D) : Enriched rosin

The amounts of the components are shown as percentages per dry pulp.

Stirring condition:

Each stirring by a propeller stirrer was carried out at 200 r.p.m for 30 seconds after each addition of each of components (A^9), (B^9), (C), (D).

Table 23:(Reference)

Order of addition: Components $(B^9) \rightarrow (D) \rightarrow (C)$

(A^9)%	(B^9)%	(D)%	(C)%	Bursting factor
0	0.1	1.0	2.0	3.31
0	0.15	1.0	2.0	3.58
0	0.2	1.0	2.0	3.79
0	0.3	1.0	2.0	4.02

Table 24:(Reference)

Order of addition: Components $(D) \rightarrow (B^9) \rightarrow (C) \rightarrow (A^9)$

(D)%	(B^9)%	(C)%	(A^9)%	Bursting factor
1.0	0.15	2.0	0.03	3.60
1.0	0.15	2.0	0.06	3.64
1.0	0.15	2.0	0.1	3.70

Table 25:(Invention)

Order of addition: Components $(A^9) \rightarrow (B^9) \rightarrow (D) \rightarrow (C)$:

(A^9)%	(B^9)%	(D)%	(C)%	Bursting factor
0.03	0.1	1.0	2.0	3.61
0.15	0.1	1.0	3.0	3.43
0.06	0.1	1.0	2.0	3.81
0.1	0.1	1.0	2.0	4.05
0.03	0.15	1.0	2.0	3.94
0.06	0.15	1.0	2.0	4.18
0.1	0.15	1.0	2.0	4.43

Note: The ion equivalent of A^9 to B^9 is 50 % in the case of $\overline{A}^9 = 0.015\%$ and $B^9 = 0.1\%$

Example 11:

The process of Example 10 was repeated under the following conditions. The results are shown in Tables 26 to 28.

Water soluble cationic polymer (A^{10}):

Copolymer of 70 mole % of acrylamide component and 30 mole % of dimethylamino ethyl methacrylate component

Viscosity : 53,000 cps (10% aq.)

Water soluble anionic polymer (B^{10}):

Partially hydrolyzed product of polyacrylamide

Hydrolyzed component: 20 mole %

Viscosity: 12,500 cps (10 % aq.)

Aluminum sulfate (C): Solid aluminum sulfate

Sizing agent (D) : Enriched rosin

Table 26:(Reference)

Order of addition: Components (D)⟶(B^{10})⟶(C)⟶(A^{10})

(D)%	(B^{10})%	(C)%	(A^{10})%:	Bursting factor
1.0	0.2	2.0	0.03	3.71
1.0	0.2	2.0	0.06	3.77
1.0	0.2	2.0	0.1	3.80

Table 27:(Reference)

Order of addition: Components (B^{10})⟶(D)⟶(C)

(A^{10})%	(B^{10})%	(C)%	(D)%	Bursting factor
0	0.1	1.0	2.0	3.45
0	0.2	1.0	2.0	3.67
0	0.3	1.0	2.0	3.86

Table 28:(Invention)

Order of addition: Components (A^{10})⟶(B^{10})⟶(D)⟶(C)

(A^{10})%	(B^{10})%	(D)%	(C)%	Bursting factor
0.03	0.1	1.0	2.0	3.71
0.06	0.1	1.0	2.0	3.83

0.1	0.1	1.0	2.0	4.19
0.03	0.2	1.0	2.0	3.88
0.06	0.2	1.0	2.0	4.09
0.1	0.2	1.0	2.0	4.33

Note: The ion equivalent of (A^{10}) to (B^{10}) is 35 % in the case of A^{10} = 0.03 % and B^{10} = 0.1 %.

Example 12:

The process of Example 10 was repeated under the following conditions and the relative bursting strength was measured, by Japanese Industrial Standard.

Water soluble cationic polymer (A^{11}):

The reaction product of epichlorohydrin, dimethylamine and hexamethylene diamine

Viscosity : 12 cps. (10% aq.)

Water soluble anionic polymer (B^{11}):

Copolymer of 85 mole % of acrylamide component and 15 mole % of sodium acrylate component

Viscosity : 6.300 cps (10% aq.)

Sizing agent (C): Enriched rosin

Aluminum sulfate (D): Solid aluminum sulfate

Table 29: (Reference)

Order of addition: Components (D) $\rightarrow$ (B^{11}) $\rightarrow$ (C) $\rightarrow$ (A^{11})

(D)%	(B^{11})%	(C)%	(A^{11})%	Bursting factor
1.0	0.2	2.0	0.06	3.66
1.0	0.2	2.0	0.09	3.70

Table 30

Order of addition: Components (A^{11}) $\rightarrow$ (B^{11}) $\rightarrow$ (D) $\rightarrow$ (C)

(A^{11})%	(B^{11})%	(D)%	(C)%	Bursting factor
0	0.1	1.0	2.0	3.40
0	0.2	1.0	2.0	3.62
0	0.3	1.0	2.0	3.85
0.03	0.15	1.0	2.0	3.83
0.06	0.15	1.0	2.0	3.98

Note: The ion equivalent of (A^{11}) to (B^{11}) in the case of A = 0.03 % and B = 0.15%.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for manufacturing paper having improved dry strength which comprises mixing an essentially alum free pulp slurry with a water soluble cationic polymer, subsequently adding a water soluble anionic polymer to the essentially alum free slurry and then making the paper from the composition obtained.

2. A process according to Claim 1 wherein the water soluble cationic polymer has a viscosity of greater than about 5 cps. as a 10% aqueous solution at 25°C.

3. A process according to Claim 2 wherein the water soluble cationic polymer has a viscosity of greater than about 100 cps. as a 10% aqueous solution at 25°C and a cation content of greater than about 1.0 gram ion/Kg. polymer.

4. A process according to Claim 2 wherein the water soluble cationic polymer has a viscosity in a range of 5 up to 100 cps. as a 10% aqueous solution at 25°C and a cation content of greater than about 3.0 gram ion/Kg. polymer.

5. A process according to Claim 1, 2 or 3 wherein the amount of the water soluble cationic polymer is more than about 0.01% by weight to the dry pulp.

6. A process according to Claim 1, 2 or 3 wherein the amount of the water soluble anionic polymer is more than about 0.1% by weight to the dry pulp.

7. A process according to Claim 1, 2 or 3 wherein the ratio of the water soluble cationic polymer to the water soluble anionic polymer is more than about 10 mole % as ion equivalent.

8. A process according to Claim 1, 2 or 3 wherein the water soluble cationic polymer is selected from the group consisting of homopolymers and copolymers of dimethyl diallyl ammonium chloride and polyethyleneimine.

9. A process according to Claim 1, 2 or 3 wherein the water soluble cationic polymer is a polyacrylamide partial Mannich reaction product produced by reacting polyacrylamide with formaldehyde and dimethylamine and a quaternary ammonium salt thereof.

10. A process according to Claim 1, 2 or 3 wherein the water soluble cationic polymer is a copolymer of acrylamide and an acrylate or methacrylate having the formula

$$CH_2{=}\overset{\displaystyle R}{\overset{|}{C}}{-}COO{-}Y{-}N\begin{matrix} \diagup R^1 \\ \diagdown R^2 \end{matrix}$$

wherein R represents hydrogen atom or methyl group; R^1 and R^2 are the same or different and represent an alkyl group, and Y represents an alkylene group having 2 or more of carbom atoms or hydroxyalkylene group having 2 or more of carbon atoms; or a quaternary ammonium salt of said copolymer.

11. A process according to Claim 1, 2 or 3 wherein the water soluble cationic polymer is a polycondensate of an epihalohydrin and at least one of monoamines, polyamines, amide amines and polyamide amines.

12. A process according to Claim 1, 2 or 3 wherein the water soluble cationic polymer is a polycondensate of epichlorohydrin and ethylenediamine or a polycondensate of epichlorohydrin, dimethylamine and pentaethylenehexamine.

13. A process according to Claim 1, 2 or 3 wherein the water soluble anionic polymer is a polyacrylamide partially hydrolyzed product or copolymer of acrylamide and acrylic acid.

14. A process according to Claim 1, 2 or 3 in which alum is added after the addition of the water soluble anionic polymers thereby improving the retention of the cationic and anionic polymers in the pulp.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente